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54. Title of the Invention

A Method of Analyzing Impurities on the Surface of Semiconductor Substrate

(54) [Title of Invention] A Method of Analyzing Impurities on the Surface of Semiconductor Substrate

(57) [Summary]

[Purpose] The purpose of the invention is to analyze the impurities present on the surface of semiconductor substrate with high degree of precision and sensitivity.

[Composition] Aqueous solution or vaporized HF is supplied from line 15, and aqueous solution or gaseous O₃ is supplied from line 16 to form a dissolving solution 17 of HF and O₃ on the surface of semiconductor substrate 12. The semiconductor substrate 12 is put in motion, such as rotation, by a driving mechanism 14 causing the dissolving solution 17 to roll on the surface of the semiconductor substrate 12. Consequently, the impurity present on the surface of the semiconductor substrate 12 is dissolved by the dissolving solution 17. The dissolving solution 17 is then collected by a pipette, and analyzed by a flameless atomic absorption apparatus. By having HF and O₃ contained in the dissolving solution 17, oxide film is efficiently formed on the semiconductor substrate surface 12 by the oxidation power of O₃. The impurity on the semiconductor substrate surface is incorporated into the oxide film. The oxide film is then dissolved by the dissolving power of HF without etching the semiconductor substrate 12. Consequently, the type and quantity of the impurity adhered to the surface of semiconductor substrate 12 can be measured with high degree of accuracy and sensitivity.

[Scope of Patent Claims]

[Claim 1] A method of analyzing impurity on the semiconductor substrate surface comprises; a processing step to create a dissolving solution containing HF and O₃ on the surface of semiconductor substrate, and a processing step to roll the solution on the semiconductor substrate surface to make contact. It also comprises a processing step to analyze said dissolving solution to measure the type and quantity of the impurity adhered to the semiconductor substrate surface. These are the characteristics of the method of analyzing impurity on the semiconductor substrate surface.

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¹ ILC Note – An alternative way of reading this name is "Norisuke."

[Claim 2] The dissolving solution containing HF and O₃, mentioned above, is created by mixing gaseous O₃ with either aqueous solution of HF or vaporized HF. These are the additional characteristics of the method of analyzing impurity on the semiconductor substrate surface described in Claim 1 of the Scope of Patent Claims.

[Claim 3] The dissolving solution containing HF and O₃, mentioned above, is created by mixing aqueous solution of O₃ with either aqueous solution of HF or vaporized HF. These are the additional characteristics of the method of analyzing impurity on the semiconductor substrate surface described in Claim 1 of the Scope of Patent Claims.

[Claim 4] A method of analyzing impurity on the semiconductor substrate surface comprises; a processing step to drip a dissolving solution containing HF and O₃ on the surface of semiconductor substrate, and a processing step to roll the solution on the semiconductor substrate surface to make contact. It also comprises a processing step to analyze said dissolving solution to measure the type and quantity of the impurity adhered to the semiconductor substrate surface. These are the characteristics of the method of analyzing impurity on the semiconductor substrate surface.

[Detailed Explanation of the Invention]

[0001]

[Areas of Industrial Application] This invention relates to a method of analysis that measures the type and quantity of impurities adhered to the surface of semiconductor substrate.

[0002]

[Prior Art] Higher level of performances, such as higher degree of integration, higher speed, greater number of functions, and higher reliability, are always demanded of ICs. To solve these issues, multitude of technologies have been introduced into hundreds of production work steps employed in the production of IC. One such technology is a technology to prevent impurities from entering the semiconductor substrate, composed of silicon (SI) as raw material, prior to the work step producing a device. As well known, prevention of impurities from entering the semiconductor substrate is indispensable in improving the device characteristics of ICs. To realize this objective, accurate analysis of the degree of contamination on the surface of semiconductor substrate is necessary.

[0003] Generally, the impurities entering the semiconductor substrates include organic substances, gas impurities, and metals. As a means of analyzing primarily metal, a method of measuring the type and quantity of impurities using a flameless atomic absorption apparatus is well known. In this method, the impurities adhered to the surface of semiconductor substrate and the impurities contained in a natural oxide film formed on the surface of semiconductor are dissolved with HF vapor. The dissolving solution is then collected to measure the type and quantity of the impurities contained with the flameless atomic absorption apparatus.

[0004] In this method, however, impurities such as aluminum (Al), or iron (Fe) can be dissolved easily with vaporized HF, but impurities of heavy metals such as copper (Cu), and gold (Au), are difficult to dissolve. Therefore, accurate quantitative analysis could not be made for these metals.

[0005] As a means to overcome these shortcomings, the following method of analysis has been devised. In this method, a dissolving solution containing HF and H₂O₂ (TN: Possibly a typo of H₂O₂) or a dissolving solution containing HF and HNO₃ is dripped on the surface of semiconductor substrate. The semiconductor substrate is put in motion so that the dissolving solution makes contact with the surface of substrate. Thus, the impurities contained in the natural oxide film formed on the semiconductor surface and the impurities adhered to the surface of semiconductor substrate are dissolved. The dissolving solution is collected to measure the type and quantity of the impurity contained with a flameless atomic absorption apparatus.

[0006] When a dissolving solution containing HF and H₂O₂ is used, the concentration of H₂O₂ must be made sufficiently high to dissolve the heavy metal impurity such as Cu into the dissolving solution in order to accurately detect it. However, when the concentration of H₂O₂ is made high, the surface of semiconductor substrate becomes hydrophilic. Consequently, it becomes difficult to roll the dissolving solution. Additionally, the collection of dissolving solution to make the measurement also becomes difficult. These problems have hindered the improvement of the accuracy of analysis results.

[0007] In addition, when a dissolving solution containing HF and HNO₃ is used, the concentration of HNO₃ must also be increased to accurately detect the Cu. However, when the concentration of HNO₃ is increased, etching occurs reaching the interior of the semiconductor substrate. This dissolves the impurities in the interior of the semiconductor substrate. Therefore, it has been unsuitable for the analysis of the type and quantity of impurities adhered to the surface of semiconductor substrate.

[0008]

[Problems to Be Solved by the Invention] As described above, the method of conventional technology using a dissolving solution containing HF and H₂O₂ causes the semiconductor substrate to become hydrophilic, and makes it difficult to roll the solution. The method of using a dissolving solution containing HF and HNO₃ causes etching of the interior of the semiconductor substrate. Consequently, it is difficult by either method, to accurately measure the type and quantity of the impurities adhered to the semiconductor substrate surface. The purpose of this invention is to present a method that solves the problems described above, and analyzes the type and quantity of impurity adhered to the semiconductor substrate surface with high degree of accuracy and sensitivity.

[0009]

[Means to Solve the Problems] In order to accomplish the purpose stated above, the method of analyzing the impurities on the semiconductor substrate surface of this invention is characterized by the following processing steps. The method comprises a processing step to create a dissolving solution containing HF and O₃ on the surface of semiconductor substrate, and a processing step to roll the dissolving solution on the semiconductor substrate surface to make contact. It also comprises a processing step to analyze said dissolving solution to measure the type and quantity of the impurity adhered to the semiconductor substrate surface.

[0010] Additionally, the dissolving solution containing HF and O₃, mentioned above, is characterized by being created by mixing gaseous O₃ with either an aqueous solution of HF or vaporized HF.

Additionally, the dissolving solution containing HF and O₃, mentioned above, is characterized by being created by mixing aqueous solution of O₃ with either an aqueous solution of HF or vaporized HF.

[0011] In addition, the method of analyzing impurity on the semiconductor substrate surface of this invention is characterized by the following composition. The method comprises a processing step to drip dissolving solution containing HF and O₃ on the surface of semiconductor substrate. It also comprises a processing step to roll the dissolving solution on the semiconductor substrate surface to make contact, and a processing step to measure the type and quantity of the impurity adhered to the semiconductor substrate surface.

[0012]

[Operation] In the analyzing method of this invention, a solution containing HF and O₃ is rolled on the surface of the semiconductor substrate to make contact so that the impurities present on the surface of semiconductor substrate is dissolved into the dissolving solution.

[0013] The process of this dissolving can be inferred to take place as follows. First, the dissolving solution containing HF and O₃ efficiently forms an oxide film on the surface of the semiconductor substrate by the oxidation power of O₃. The impurities adhered to the surface of the semiconductor substrate is incorporated into the oxide film. However, the oxidation power of O₃ deteriorates rapidly. Consequently, the dissolving power of HF becomes stronger after a short time, and dissolves the oxide film, as the oxidation power is dissipated. In addition, the dissolving solution containing HF and O₃ has a slower rate of etching the semiconductor substrate than the dissolving solution containing HF and HNO₃. Consequently, the dissolving solution containing HF and O₃ can dissolve the impurities on the semiconductor substrate surface efficiently without dissolving the impurities contained in the interior of the semiconductor substrate.

[0014]

[Embodiment] The embodiment of the invention will be explained in the following referring to the figures. The first embodiment of the invention is shown in Figure 1. An apparatus is shown that realizes a method of analyzing impurities adhered to the surface of semiconductor substrate by creating a dissolving solution, by supplying vaporized HF and gaseous O₃, and analyzing the impurities adhered to the semiconductor substrate surface. The apparatus comprises a table 13 that holds a semiconductor substrate, composed of Si as raw material, in a chamber 11, as shown in Figure 1. It also comprises, a driving mechanism 14 that provides motion to the semiconductor substrate 12, a line 15 that supplies vaporized HF, and a line 16 that supplies gaseous O₃. When the measurement is made, the semiconductor substrate, composed of Si as raw material, is placed on the table 13 in the chamber 11, and vaporized HF and gaseous O₃ is supplied onto the surface of the semiconductor substrate 12.

[0015] The vaporized HF and gaseous O₃ reacts chemically after being exposed to air, and a dissolving solution 17 is created after being liquefied. Next, the semiconductor substrate 12 is rotated by the driving mechanism 14, while shifting the horizontal surface, so that the solution 17 is rolled around on the semiconductor substrate 12 to make contact. The impurities contained in the natural oxide film formed on the surface of semiconductor substrate 12, and the impurities adhered to the surface of semiconductor substrate 12 are incorporated into the dissolving solution 17.

[0016] The following events are inferred to take place in this dissolving process. First, the dissolving solution 17 containing HF and O₃ efficiently oxidizes the surface of the semiconductor substrate 12 by the oxidizing power of O₃ contained in the dissolving solution 17. The oxide film formed contains the impurities adhered to the surface of the semiconductor substrate 12. However, the oxidizing power of O₃ contained in the dissolving solution 17 deteriorates rapidly, giving way to the HF's dissolving power of the oxide film, as time elapses. The natural oxide film and the oxide film formed are dissolved. Then, the dissolving solution 17 is collected with a pipette, and measurement is made for the type and quantity of the impurities contained with a flameless atomic absorption apparatus. Alternatively, the dissolving solution 17 can be dried on the semiconductor substrate 12 without being collected, and analyzed with a total reflection X-ray analysis.

[0017] The results of experiment performed actually using a dissolving solution containing HF and O₃ will be explained, particularly noting the (1) solubility of Cu which is the heavy metal impurity, and (2) the etching rate of the Si substrate.

[0018] (1) An Si substrate on which 6×10^{12} (atoms / cm²) of Cu is adhered is soaked for three minutes under normal temperature in a dissolving solution containing 0.2 % concentration of HF and 1 to 10 ppm concentration of O₃. The dissolving solution dissolved approximately 4.00 to 5.90 ($\times 10^{11}$ atoms / cm²) of Cu. On the other hand, when an Si substrate with identical condition is soaked in a dissolving solution containing 0.2 % concentration of HF and 0.1 to 10% concentration of H₂O₂, approximately 5.70 to 5.95 ($\times 10^{12}$ atoms / cm²) of Cu was dissolved. Clearly, the dissolving solution containing HF and O₃ recovers Cu more efficiently than in the past. (TN: Possible typos in the figures (?)

[0019] (2) The etching rate of Si substrate by the dissolving solution containing approximately 0.05 to 0.5 % concentration of HF and approximately 2 ppm concentration of O₃ is approximately 3 to 17 (A / min). The etching rate of Si substrate by a solution containing approximately 0.02 to 4% concentration of HF and approximately 68% concentration of HNO₃ is approximately 100 to 6000 (A / min). The etching of Si substrate can be suppressed more than the conventional method by using a solution containing HF and O₃.

[0020] Next, the second embodiment will be explained. The second embodiment of this invention is shown in Figure 2. An apparatus that realizes a method of analyzing impurities adhered to the surface of semiconductor substrate where a dissolving solution is created by supplying aqueous solution of HF and aqueous solution of O₃, is shown. As shown in Figure 2, the apparatus comprises a table 23 that holds the semiconductor substrate 22, composed of Si as raw material, placed in a chamber 21. It also comprises, a driving mechanism 24 that provides motion to the semiconductor substrate 22, a line 25 supplying aqueous solution of HF, and a line 26 supplying aqueous solution of O₃.

[0021] When a measurement is made, the semiconductor substrate 22 is placed on the table 23. The aqueous solution of HF and aqueous solution of O₃ is supplied onto the surface of semiconductor substrate 22 to create a dissolving solution 27. Next, the semiconductor substrate 22 is rotated by a driving mechanism 24 while shifting the horizontal surface, so that the dissolving solution 27 is rolled around on the semiconductor substrate 22 to make contact. The impurities contained in the natural oxide film formed on the surface of the semiconductor substrate 22 and the impurities adhered to the surface of the semiconductor substrate 22 are incorporated into the dissolving solution 27. Then, the dissolving solution 27 is collected by a pipette, and the type and quantity of the impurities are measured by a flameless atomic absorption apparatus. Alternatively, the solution 17 can be dried on the semiconductor substrate 12 without being collected, and analyzed with a total reflection X-ray analysis.

[0022] In the two embodiments described above, the dissolving solution containing HF and O₃ has been created on the surface of the semiconductor substrate 22. However, the dissolving solution 27 containing HF and O₃ can be prepared ahead of time, and dripped onto the semiconductor substrate 22 to make measurement.

[0023] In the two embodiments described above, the semiconductor substrate analyzed were composed of Si. However, the application of this invention is not limited to semiconductor substrates composed of Si, any other semiconductor, such as chemical compound semiconductor can be used. Additionally, in the first and second embodiments shown above, the line supplying vaporized HF or aqueous solution of HF, and the line supplying gaseous O₃ or aqueous solution of O₃ are not limited to the number and positions described in Figures 1 and 2. Any other configuration producing the dissolving solution 27 would be acceptable.

[0024] Additionally, as for the timing of supplying vaporized HF or aqueous solution of HF, and gaseous O₃ or aqueous solution of O₃, the dissolving solution 27 can be created more efficiently when both substances are supplied simultaneously. It is effective in producing the dissolving solution 27 more quickly. When vaporized HF or aqueous solution of HF is supplied first, the vaporized HF or aqueous solution of HF dissolves the impurities on the surface of the semiconductor substrate 22, exposing the surface of the semiconductor substrate

22. Since the semiconductor substrate surface 22 itself shows hydrophobic property, the effect of making the solution easier to roll around on the surface of semiconductor substrate 22 can be obtained.

[0025] In the creation of dissolving solution 27, an example of supplying both HF and O₃ in gaseous state, and an example of supplying both in aqueous solutions were cited in the embodiments. However, the dissolving solution 27 can be created by supplying either one of the substances in gaseous state and the other in aqueous solution. Additionally, a method of preparing the dissolving solution 27 containing a mixture of HF and O₃ ahead of time, and dripping it onto the surface of the semiconductor substrate 22 would be acceptable. In other words, so long as a substance containing HF and O₃ is created on the surface of the semiconductor substrate 22, the process of its creation does not matter.

[0026] However, O₃ decomposes rapidly in aqueous solution. Consequently, the oxidizing power of O₃ diminishes in relatively short time. Therefore, it is preferable to prepare the aqueous solution of O₃ immediately before the measurement is made. When a solution 27 containing a mixture of HF and O₃ is prepared ahead of time, and dripped onto the surface of semiconductor substrate 22, it is also preferable to prepare it immediately before the measurement is made.

[0027] As for the means of rolling the dissolving solution 27 on the surface of semiconductor substrate 22, it is not limited to the method described in the embodiment. For example, there is a method where a jig resembling a dropping pipette, holding the dissolving solution 27, is placed in contact with the surface of the semiconductor substrate 22. Then, as the semiconductor substrate 22 is rotated, the dropping pipette is simultaneously moved horizontally, dissolving the impurities attached to the surface of the semiconductor substrate 22 into the dissolving solution 27.

[0028] The measurement method is not limited to the analysis method using a flameless atomic absorption apparatus or a total reflection X-ray analysis. Any method capable of determining the type and quantity of the atoms of impurities dissolved in the dissolving solution 27 would be acceptable. For example, mass spectrometry analysis by means of inductive coupling plasma (ICP) may be used.

If it is necessary to collect the dissolving solution 27, the semiconductor substrate 22 can be tilted to collect the dissolving solution 27. The means of accomplishing the collection does not matter.

[0029]

[Effects of the Invention] The method of analyzing the impurities on the surface of semiconductor substrate of this invention can measure the type and quantity of the impurities adhered to the surface of semiconductor substrate with high degree of accuracy and sensitivity.

[Brief Explanation of the Drawings]

[Figure 1] This is the first embodiment of the invention. An apparatus that realizes a method of analyzing the impurities adhered to the surface of semiconductor substrate, utilizing a dissolving solution created by supplying vaporized HF and gaseous O₃ is shown.

[Figure 2] This is the second embodiment of this invention. An apparatus that realizes a method of analyzing the impurities adhered to the surface of semiconductor substrate, utilizing a dissolving solution created by supplying aqueous solution of HF and aqueous solution of O₃ is shown.

[Explanation of Symbols]

11, 21. Chamber

12, 22. Semiconductor substrate

13, 33. Table

14, 24. Driving mechanism

15. Supply line of vaporized HF

16. Supply line of gaseous O₃

17, 27. A drop of dissolving solution of HF and O₃

25. Supply line of aqueous solution of HF

26. Supply line of aqueous solution of O₃

CHAR LEGENDS

[Figure 1]

[Figure 2]

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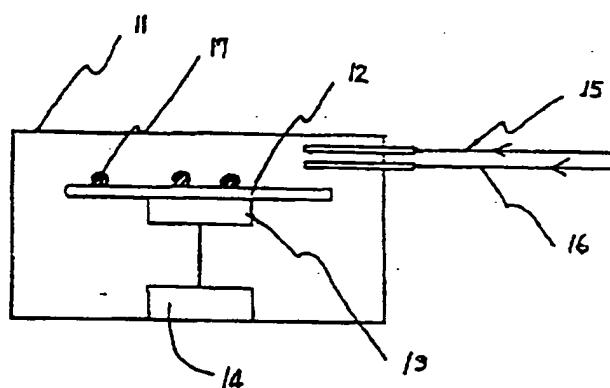
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(54)【発明の名称】 半導体基板表面の不純物分析方法

(57)【要約】

【目的】 半導体基板表面上の不純物を高感度かつ高精度に分析することにある。

【構成】 ライン15よりHF水溶液または蒸気を、ライン16よりO₃水溶液またはガスを供給して、半導体基板表面12上にHFとO₃の溶解液17を形成し、この半導体基板12を駆動機構14で回転等の運動をさせることにより、溶解液17を半導体基板12表面上において転がす。半導体基板12表面上にあった不純物は溶解液17により溶解される。この溶解液17をピペット等により採集して、フレームレス原子吸光装置で分析する。溶解液17にHFとO₃を含ませることにより、O₃の酸化力により半導体基板12表面上に酸化膜を効率良く形成し、半導体基板12表面上の不純物を酸化膜に取り込む。その後HFの溶解力により、半導体基板12をエッチングすることなく、酸化膜を溶解するため、半導体基板12表面に付着した不純物の種類及び量の測定を、高感度かつ高精度に行うことができる。



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【特許請求の範囲】

【請求項1】 半導体基板表面上にHFとO₃とを含む溶解液を生成する工程と、この溶解液を前記半導体基板表面と接触する様に移動させる工程と、この移動させた溶解液を分析し前記半導体基板表面に付着していた不純物の種類および量を測定する工程とを有することを特徴とする半導体基板表面の不純物分析方法。

【請求項2】 上記HFとO₃とを含む溶解液は、HF水溶液またはHF蒸気のいずれか一方と、O₃ガスを混在させることによって生成することを特徴とする請求項1記載の半導体基板表面の不純物分析方法。

【請求項3】 上記HFとO₃とを含む溶解液は、HF水溶液またはHF蒸気のいずれか一方と、O₃水溶液を混在させることによって生成することを特徴とする請求項1記載の半導体基板表面の不純物分析方法。

【請求項4】 半導体基板表面上にHFとO₃とを含む溶解液を滴下する工程と、この溶解液を前記半導体基板表面と接触する様に移動させる工程と、この移動させた溶解液を分析し前記半導体基板表面に付着していた不純物の種類および量を測定する工程とを有することを特徴とする半導体基板表面の不純物分析方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は、半導体基板表面上に付着している不純物の種類及び量を測定する分析方法に関する。

【0002】

【従来の技術】ICは、常に高集積、高速性、多機能性、高信頼性がもとめられている。そして、これらの課題を解決するため、数百にわたるICの生産工程ごとに、様々な技術が導入されている。その1つが、デバイスを形成する工程の前において、シリコン(Si)等を材料とする半導体基板への不純物混入を防ぐ技術である。すでに周知のとおり、ICのデバイス特性の向上には、半導体基板への不純物の混入の抑制は不可欠であり、その実現化には、半導体基板表面上の汚染度の正確な分析が必要とされる。

【0003】一般に、半導体基板に混入する不純物には有機物、ガス不純物、金属などがある。このうち主に金属を測定対象としている分析方法として、半導体基板表面に付着した不純物及び半導体基板表面に形成された自然酸化膜内に含まれる不純物をHF蒸気で溶解し、その溶解液を採集してフレームレス原子吸光装置で不純物の種類及び量を測定する方法が知られている。

【0004】しかし、この方法では、HF蒸気によりアルミニウム(Al)、鉄(Fe)等の不純物は溶解するが、銅(Cu)、金(Au)などの重金属不純物は溶解しにくく、正確に定量分析を行うことができなかった。

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体基板表面上にHFとH₂O₂を含む溶解液、又は、HFとHNO₃を含む溶解液を滴下し、その溶解液を半導体基板と接するように移動させることにより、半導体基板表面に付着した不純物及び半導体基板表面に形成された自然酸化膜内に含まれる不純物を溶解させ、その溶解液を採集してフレームレス原子吸光装置で不純物の種類及び量を測定する。

【0006】HFとH₂O₂を含む溶解液を用いた場合には、重金属不純物例えはCuを正確に検出するためには、H₂O₂濃度を高くして、溶解液にCuを溶解する必要がある。しかし、H₂O₂濃度を高くすると半導体基板表面は親水性となり、溶解液を移動させにくくなり、さらには測定のために採集することも困難となる。従って、分析結果の精度の向上が望めない問題を有していた。

【0007】また、HFとHNO₃を含む溶解液を用いた場合も、Cuを正確に検出するためには、HNO₃濃度を高くしなければならない。しかし、HNO₃濃度を高くすると、半導体基板内部までエッチングされ、半導体基板内部の不純物が溶解してしまい、半導体基板表面に付着している不純物の種類及び量に関する分析には不適切であった。

【0008】

【発明が解決しようとする課題】以上説明したように、従来技術のHFとH₂O₂を含む溶解液を用いた方法では、半導体基板表面上が親水性となり、溶解液の移動が困難になる。HFとHNO₃を含む溶解液を用いた方法では、半導体基板内部をエッチングする。従って、いずれの方法においても、半導体基板表面の不純物の種類および量を正確に測定することは難しい。そこで、本発明は、上記問題を解決し、半導体基板表面上に付着している不純物の種類及び量を高感度及び高精度に分析することを目的とする。

【0009】

【課題を解決するための手段】上記目的を達成するために、本発明の半導体基板表面の不純物分析方法では、半導体基板表面上にHFとO₃とを含む溶解液を生成する工程と、この溶解液を前記半導体基板表面と接触する様に移動させる工程と、この移動させた溶解液を分析し前記半導体基板表面に付着していた不純物の種類および量を測定する工程とを有することを特徴とする。

【0010】尚、上記HFとO₃とを含む溶解液は、HF水溶液またはHF蒸気のいずれか一方と、O₃ガスを混在させることによって生成することを特徴とする。尚、上記HFとO₃とを含む溶解液は、HF水溶液またはHF蒸気のいずれか一方と、O₃水溶液を混在させることによって生成することを特徴とする。

と接触する様に移動させる工程と、この移動させた溶解液を分析し前記半導体基板表面に付着していた不純物の種類および量を測定する工程とを有することを特徴とする。

【0012】

【作用】本発明の分析方法では、HFとO₃を含む溶解液を半導体基板表面と接触するように移動させることにより、この溶解液中に半導体基板表面に存在する不純物を溶解させる。

【0013】この溶解過程は次のように考えられる。最初に、HFとO₃を含む溶解液は、O₃の酸化力より半導体基板表面に酸化膜を効率良く形成し、半導体基板表面上の不純物を酸化膜内に取り込む。しかし、O₃の酸化力は劣化しやすいため、しばらくするとその劣化に伴いHFの溶解力の方が勝り、酸化膜が溶解する。また、HFとO₃を含む溶解液は、HFとHNO₃を含む溶解液に比べ、半導体基板のエッチング速度が遅い。このため、半導体基板内部に含まれる不純物を溶解することなく、HFとO₃を含む溶解液は、能率良く半導体基板表面上の不純物を溶解できる。

【0014】

【実施例】以下、図面を参照して本発明を実施例により説明する。図1は、本発明の第一の実施例であり、HF蒸気とO₃ガスを供給することによって溶解液を生成し、半導体基板表面上の不純物を分析する方法を実現させる装置を示す。図1のとおり、この装置はチャンバー11内に、Siを材料とした半導体基板12を固定し支える支持台13と、半導体基板12に運動を与える駆動機構14と、HF蒸気を供給するライン15と、O₃ガスを供給するライン16を有している。測定を行う際には、チャンバー11内において、支持台13にSiを材料とする半導体基板12を設置し、半導体基板12表面上にHF蒸気とO₃ガスを供給する。

【0015】HF蒸気とO₃ガスは空気に入れ化学反応を起こし、その後液化することにより溶解液17を生成する。次に、駆動機構14により半導体基板12を水平面を変えながら回転させ、溶解液17を半導体基板12と接するようにならぶ。半導体基板12表面上に付着した不純物及び半導体基板12表面上に形成された自然酸化膜内に含まれる不純物は、溶解液17中に取り込まれる。

【0016】この溶解の過程には次の様なことが生じていると考えられる。まず、HFとO₃を含む溶解液17は、溶解液17中のO₃の酸化力から半導体基板12表面を効率良く酸化する。この時形成した酸化膜は、半導体基板12表面に付着していた不純物を含んでいる。しかし、溶解液17中のO₃の酸化力は劣化しやすく、時間がたつにつれHFの酸化膜溶解力が勝り、自然酸化膜及び形成された酸化膜を溶解する。その後、ピペット等により、

集することなく半導体基板12上で乾燥させてから全反射光X線分析を行う。

【0017】ここで、実際にHFとO₃を含む溶解液を使用した実験結果について、(1) 重金属不純物であるCuの溶解度、(2) Si基板のエッチング速度に着目して説明する。

【0018】(1) 6×10^{12} (atoms/cm²) のCuが付着しているSi基板を、0.2%濃度のHFと1~10ppm濃度のO₃を含む溶解液に常温にて3分間ひたす。溶解液は、Cuを約4.00~5.90 ($\times 10^{11}$ atoms/cm²) 溶解した。これに対し、0.2%濃度のHFと0.1~10%濃度のH₂O₂を含む溶解液に同条件のSi基板をひたすと、Cuを約5.70~5.95 ($\times 10^{12}$ atoms/cm²) 溶解する。明らかに、HFとO₃を含む溶解液は、従来よりCuを効率良く回収している。

【0019】(2) 約0.05~0.5%濃度のHFと約2ppm濃度のO₃を含む溶解液によるSi基板をエッチングする速度は、約3~17 (A/min.) である。約0.02~4%濃度のHFと約68%濃度のHNO₃を含む溶解液によるSi基板をエッチングする速度は、約100~6000 (A/min.) である。HFとO₃を含む溶解液を用いることにより、従来よりSi基板のエッチングは進ますにすむ。

【0020】次に第2の実施例について述べる。図2は、本発明の第二の実施例である。HF水溶液とO₃水溶液を供給することによって溶解液を生成し、半導体基板表面上の不純物を分析する方法を実現させる装置を示す。図2のとおり、この装置は、チャンバー21内に、Siを材料とした半導体基板22を固定し支える支持台23と、半導体基板22に運動を与える駆動機構24と、HF水溶液を供給するライン25と、O₃水溶液を供給するライン26を有している。

【0021】測定を行う際には、支持台23に半導体基板22を設置し、半導体基板22表面上にHF水溶液とO₃水溶液を供給し、溶解液27を生成する。次に、駆動機構24により半導体基板22を水平面を変えながら回転させ、溶解液27を半導体基板22と接するようにならぶ。半導体基板22表面上に付着した不純物及び半導体基板22表面上に形成された自然酸化膜内に含まれる不純物は、溶解液27中に取り込まれる。その後、ピペット等により溶解液27を採集し、フレームレス原子吸光装置で不純物の種類及び量を測定する。もしくは、溶解液27を採集することなく半導体基板22上で乾燥させてから全反射光X線分析を行う。

【0022】尚、上記2つの実施例では、半導体基板22表面上でHF及びO₃を含む溶解液27を生成したが、HF及びO₃を含む溶解液27を事前に生成し、それを半導体基板22表面上に滴下して測定を行っても良い。

【0023】当

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の例において、HF蒸気またはHF水溶液を供給するライン、O₃ガスまたはO₃水溶液を供給するラインに関しては、その数及び位置は、図1または図2で説明したものに限定されず、溶解液27を生成すれば他の構成を使用しても良い。

【0024】又、HF蒸気またはHF水溶液及びO₃ガスまたはO₃水溶液を供給するタイミングについては、両者を同時に供給した場合、溶解液27の生成が効率良く行われ、溶解液27を早く得られる効果がある。又、HF蒸気またはHF水溶液を先に供給した場合、HF蒸気またはHF水溶液は半導体基板22表面上の不純物を溶解し、半導体基板表面22を露出させる。半導体基板表面22そのものは疎水性を示し、従って、溶解液を半導体基板22上で転がしやすい効果が得られる。

【0025】さらに、溶解液27の生成にあたり、本実施例ではHFとO₃は両者ともガス状態のものを供給する例と、両者とも水溶液状態のものを供給する例を挙げたが、どちらかがガス状態で他方が水溶液状態のものを供給して生成してもよい。又、HFとO₃を混在させた溶解液27をあらかじめ作成し半導体基板22表面に滴下してもよい。つまり、HFとO₃を含んだものが半導体基板22表面上に生成されれば、その過程は問われない。

【0026】しかし、O₃は、水溶液中では分解しやすいため、O₃のもつ酸化力が比較的短時間で弱くなる。従って、測定を行う直前でO₃水溶液を生成するのが好ましい。又、HFとO₃を混在させた溶解液27をあらかじめ作成し半導体基板22表面に滴下する場合も、測定を行う直前で供給するのが好ましい。

【0027】この他に、半導体基板22上に溶解液を転がすためにとった手段についてだが、本実施例に限らない。例えば、予め溶解液27をスポット状治具で支持しつつ半導体基板22表面に接触させ、その後、半導体基板22を回転させると共にスポット状治具を水平方向に移動さ

せることにより半導体基板22表面上に付着していた不純物を溶解液27に溶解させる方法もある。

【0028】尚、測定方法は、フレームレス原子吸光装置を用いた分析及び全反射X線分析に限定されず、不純物が溶解した溶解液27から、原子の種類及び量を決定できるものであればよい。例えば、誘導結合プラズマ(ICP)による質量分析が挙げられる。又、溶解液27を採集する必要がある場合は、半導体基板22を傾けて溶解液27を採集してもよく、その手段は問わない。

10 【0029】

【発明の効果】本発明による半導体基板表面の不純物分析方法は、半導体基板表面に付着した不純物の種類及び量の測定を、高感度かつ高精度に行うことができる。

【図面の簡単な説明】

【図1】本発明の第一の実施例である、HF蒸気とO₃ガスを供給することによって溶解液を生成し、半導体基板表面上の不純物を分析する方法を実現させる装置を示す図である。

【図2】本発明の第二の実施例である、HF水溶液とO₃水溶液を供給することによって溶解液を生成し、半導体基板表面上の不純物を分析する方法を実現させる装置を示す図である。

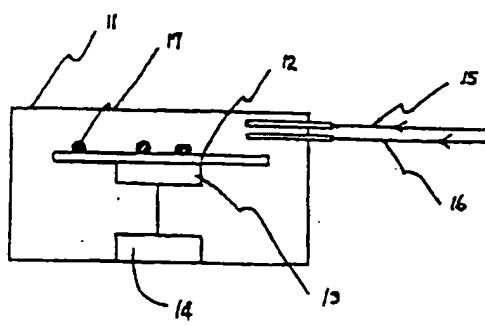
【符号の説明】

11, 21	チャンバー
12, 22	半導体基板
13, 23	支持台
14, 24	駆動機構
15	HF蒸気供給ライン
16	O ₃ ガス供給ライン
17, 27	HFとO ₃ の溶解液滴
25	HF水溶液供給ライン
26	O ₃ 水供給ライン

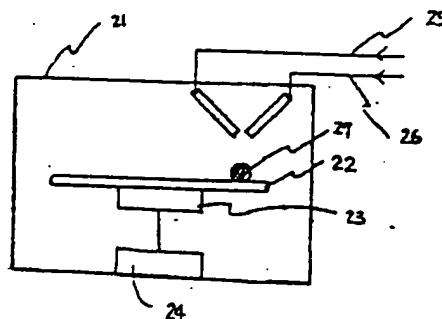
30

17, 27	HFとO ₃ の溶解液滴
25	HF水溶液供給ライン
26	O ₃ 水供給ライン

【図1】



【図2】



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